



Investigation of Ni-Al, Ni-Mg-Al and Ni-Cu-Al catalyst for hydrogen production from pyrolysis–gasification of polypropylene

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ABSTRACT

Co-precipitated nickel-based catalysts with different metallic molar ratios and calcination temperature were investigated for the production of hydrogen from the pyrolysis–gasification of polypropylene. The experiments were carried out at a pyrolysis temperature of 500 °C and gasification temperature of 800 °C in the presence of steam using a two-stage reaction system. The results suggest that with increasing Ni content in the Ni-Al or Ni-Mg-Al catalyst, the catalytic activity of the catalyst increased, in relation to hydrogen production. For example, the potential hydrogen production increased from 48.8 to 57.7 wt.%, and the amount of water reacted increased from 1.2 to 1.3 (g water/g polypropylene), when the Ni-Al molar ratio was increased from 1:4 to 1:1. After reaction in the pyrolysis–gasification process, the non-reduced Ni-Al catalyst was reduced into metallic Ni, as observed from XRD and TGA analysis. The introduction of Mg into the Ni-Al catalyst significantly increased the amount of reacted water and improved the performance of the catalyst in relation to coke formation, although the hydrogen production was not significantly improved. For the Ni-Al or Ni-Mg-Al catalyst, a 850 °C calcination temperature resulted in a lower catalytic activity compared to the lower calcination temperature of 750 °C. The substitution of Cu for Mg in the Ni-Mg-Al catalyst significantly reduced the catalytic ability for hydrogen production.

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1. Introduction

Hydrogen energy is attracting significant interest as it represents one of the most promising energy sources for the future, since its combustion only generates water. Currently, about 96% of H₂ is produced via steam methane reforming, coal gasification and oil reforming, etc. [1]. The use of alternative feedstock sources of H₂, particularly sourced from waste materials, would provide an important role in future energy scenarios. One such potential alternative source for hydrogen production is from waste plastics. Hydrogen production from the thermal decomposition of plastics has been proven to be possible by some researchers [2–4]. Waste plastics are generated in large quantities for example, it has been reported that about 19.9 million tonnes of waste plastics are generated in Western Europe each year [5].

It is known that the steam gasification and presence of a catalyst have a great effect on the hydrogen production from the thermal decomposition of plastics. Nickel-based catalysts are commonly used by researchers for hydrogen production from the thermal processing of biomass or plastics [6–9]. Noble metals such as Ru and Rh are reported to be more effective than nickel-based

catalysts, however, they are not commonly used in industry because of their high cost [10]. Ni-Al and Ni-Mg-Al catalysts have been researched during the gasification of biomass by Arauzo et al. [11,12]. Different preparations of Ni-Al catalysts were also investigated by Garcia et al. [13] for hydrogen production from the steam gasification of biomass. They reported that the rising pH technique (precipitated with NH₄OH) used in the preparation of the catalyst can be suitable for the use in the steam gasification of biomass.

In our previous study [4], it was found that Ni-Al and Ni-Mg-Al catalysts prepared by co-precipitation were effective for the production of hydrogen from pyrolysis–gasification of polypropylene. In this paper, further investigations in relation to the different molar ratios of Ni-Al in the catalyst, and the addition of Mg or Cu into the Ni-Al catalyst, at different calcination temperatures have been conducted for the production of hydrogen from pyrolysis–gasification of polypropylene using a two-stage reaction system.

2. Materials and methods

2.1. Materials

Polypropylene was obtained as 2 mm virgin polymer pellets provided by BP Chemicals UK. Zeolite ZSM-5 (CBV 8014) catalyst support was provided by Zeolyst International PA, US.

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Ni-Al and Ni-Mg-Al catalysts were prepared using the rising pH technique according to the method reported by Garcia et al. [13]. The precipitant 1 M $\text{NH}_4(\text{OH})$ was added to 200 ml of an aqueous solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with or without the addition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. The precipitation was carried out at 40 °C with moderate stirring until the final pH (7.9 for Ni-Al catalyst, 8.3 for Ni-Mg-Al catalyst, and 9.0 for Ni-Cu-Al and Ni-Cu-Mg-Al catalyst) was obtained. The precipitates were filtered with water (40 °C), followed by drying at 105 °C overnight, and then were calcined at 750 or 850 °C for 3 h. The Ni-Al molar ratios of 1:4, 1:2 and 1:1 were investigated. The Ni-Mg-Al molar ratios of 1:1:4, 1:1:2 and 1:1:1 were investigated. For the Ni-Al (1:4 and 1:1) and Ni-Mg-Al (1:1:4 and 1:1:1) catalysts, calcination temperatures of 750 and 850 °C were studied. All the catalysts used in this paper were crushed and sieved to granules with a size range between 0.065 and 0.212 mm.

2.2. Characterization of catalysts

The BET (Brunauer, Emmett and Teller) surface area of each catalyst was determined by nitrogen adsorption experiments using a Quantachrome Corporation (FL, US) Autosorb 1-C Instrument. The BET surface areas of the prepared catalysts are shown in Table 1.

Selected catalysts were analysed by X-ray diffraction (XRD). The analysis was carried out with a Philips PW 1050 Goniometer using a PW 1730 with a Cu $\text{K}\alpha$ radiation X-ray tube. The sample was ground to less than 75 μm size and loaded into the 20 mm aperture of an aluminium sample holder. The data was collected by Hiltonbrooks' HBX data acquisition software. The phase identification was obtained using GBC Scientific Equipment Ltd. TRACES software using the ICDD PDF2 (International Centre for Diffraction Data Powder Diffraction Files) database.

The temperature-programmed oxidation (TPO) of reacted catalysts was carried out using a Stanton-Redcroft thermogravimetric analyser (TGA) to determine the properties of the coked carbons deposited on the reacted catalysts. The differential thermogravimetry (DTG) results from the experiment of TPO were also discussed in this paper. About 100 mg of the reacted catalyst was heated in an atmosphere of air at 15 °C min^{-1} to a final temperature of 800 °C, with a dwell time of 10 min.

A high resolution scanning electron microscopy (SEM, LEO 1530) coupled to an energy dispersive X-ray spectrometer (EDXS) was used to characterise and examine the characteristics of the carbon deposited on the coked catalysts. Transmission electron microscopy (TEM) (Phillips CM200) coupled with EDXS was used to determine the characteristics of the Ni-Al (1:1) catalyst. For the TEM analysis, the sample was ground, dispersed with acetone, and then deposited on a Cu grid covered with a perforated carbon membrane.

2.3. Experimental system

The polypropylene (PP) was used as the raw material, as received, for the investigation of hydrogen production. The pyrolysis–gasification reactor used for hydrogen production was a two-stage batch system. A schematic diagram of the reactor and the procedure of the experimental system were presented previously [4].

During each experiment, 1 g of polypropylene and 0.5 g of catalyst were used. The pyrolysis temperature, in the first reactor and gasification temperature, in the second reactor, were 500 and 800 °C, respectively. Nitrogen was used as the carrier gas. Water was injected with a flow rate of 4.74 g h^{-1} into the second reactor, therefore passing steam through the catalyst bed (gasification) together with the pyrolysed gases derived from the thermal degradation of the polypropylene.

The gaseous products after the gasification process were passed through two condensers, where the condensed products (normally water) were collected. The non-condensed gases were collected with a 25 l Tedlar™ gas sample bag. The reproducibility of the reaction system was tested thoroughly, and experiments were repeated to ensure the reliability of research results.

The gases collected in the sample bag were analysed off-line by packed column gas chromatography (GC). C_1 to C_4 hydrocarbons were analysed using a Varian 3380 gas chromatograph with a flame ionisation detector, with a 80–100 mesh Hysep column and nitrogen carrier gas. Permanent gas (H_2 , CO , O_2 , N_2 and CO_2) were analysed by a second Varian 3380 GC with two separate columns. Hydrogen, oxygen, carbon monoxide and nitrogen were analysed on a 60–80 mesh molecular sieve column with argon carrier gas, whilst carbon dioxide was analysed on a Hysep 80–100 mesh column with argon carrier gas.

3. Results and discussion

3.1. Investigation of Ni-Al catalyst with different molar ratios

3.1.1. XRD and EDXS results of Ni-Al catalysts before and after reaction

In this paper, the Ni-Al catalyst with the molar ratios of 1:1 and 1:4 calcined at a temperature of 750 °C were analysed by XRD before and after reaction. The XRD results are shown in Fig. 1 and indicate the presence of NiO and NiAl_2O_4 in both the freshly prepared Ni-Al (1:4) and Ni-Al (1:1) catalysts. The same NiO and NiAl_2O_4 phases were reported by Clause et al. [14] from the XRD analysis of Ni-Al catalyst precursors.

From Fig. 1, compared to the fresh Ni-Al (1:4) catalyst, a higher crystallinity and proportion of NiO phase are detected for the fresh Ni-Al (1:1) catalyst which might be due to the higher ratio of Ni in

Table 1
BET surface area of the researched catalysts.

Catalyst	Initial molar ratio	Experimental molar ratio	Calcination temperature (°C)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Ni-Al	1:4	1:3.7	750	143
Ni-Al	1:2	1:1.8	750	155
Ni-Al	1:1	1:0.9	750	116
Ni-Mg-Al	1:1:4	1:0.5:4	750	97
Ni-Mg-Al	1:1:2	1:0.6:1.7	750	118
Ni-Mg-Al	1:1:1	1:0.6:1	750	99
Ni-Cu-Al	1:1:2	1:0.9:2.4	750	61
Ni-Cu-Mg-Al	1:1:1:3	1:0.9:0.8:2.6	750	76
Ni-Al	1:4	1:3.6	850	88
Ni-Al	1:1	1:0.9	850	75
Ni-Mg-Al	1:1:4	1:0.5:3.8	850	67
Ni-Mg-Al	1:1:1	1:0.5:1	850	74

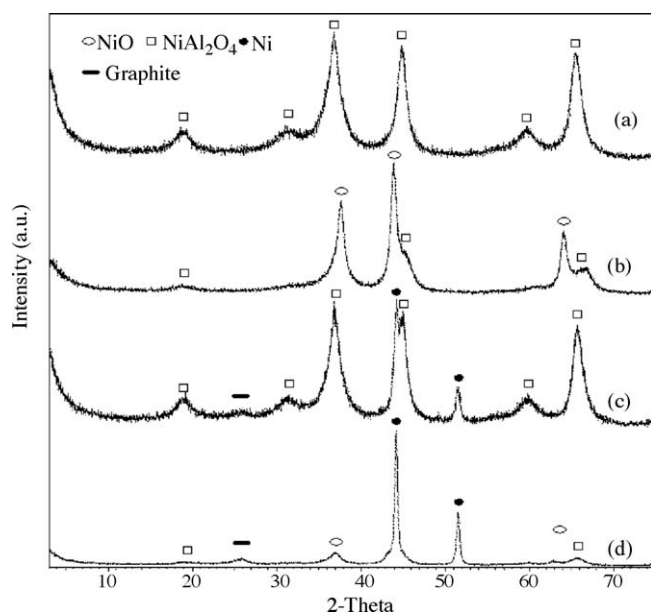


Fig. 1. XRD spectra of selected catalysts: (a) fresh Ni-Al (1:4) catalyst; (b) fresh Ni-Al (1:1) catalyst; (c) reacted Ni-Al (1:4) catalyst; (d) reacted Ni-Al (1:1) catalyst.

the catalyst. It is indicated that a metallic Ni phase was obtained after the reaction of the catalyst in the pyrolysis–gasification of polypropylene (Fig. 1(c) and (d)). It is suggested that the Ni-Al catalysts were reduced due to the reducing environment in the process. Graphite carbon was also observed for the reacted Ni-Al catalyst. Also quite a high proportion of Ni phase was found for the reacted Ni-Al (1:1) catalyst compared with the reacted Ni-Al (1:4) catalyst.

The molar ratios of prepared nickel catalysts obtained from the EDXS are shown in Table 1. The EDXS graph of the selected nickel catalysts are also shown in Fig. 2. It should be noted that the EDXS system used was a semi-quantity analysis method. The intensity of each element in the catalyst from Fig. 2 could also provide information for the composition of the catalyst. From Table 1 and Fig. 2, it seems that there is some consistency between the results of the composition from EDXS and the initial designed composition. Although some differences were observed for the composition of the catalyst from the EDXS analysis compared to the initial composition, the investigation of different Ni content in the catalyst and the addition of certain metals to the catalyst is regarded as negligible. In this paper, the prepared nickel catalysts are referred to the initial element composition.

3.1.2. Product yield and gas composition with Ni-Al catalyst in the pyrolysis–gasification of polypropylene

The Ni-Al catalysts with molar ratios of 1:4, 1:2 and 1:1 were examined for the effectiveness as catalysts for the production of hydrogen from the pyrolysis–gasification of polypropylene. The mass balance and carbon balance of the experiments is shown in Table 2. It is shown that the amount of reacted water increased from 1.2 to 1.3 (g water/g polypropylene), when the Ni-Al molar ratio was increased from 1:4 to 1:1. The calculated input oxygen from the reacted water and the output oxygen from CO and CO₂ were shown to have a good mass balance in this paper. The gas yield in relation only to the mass of polypropylene also increased with increasing Ni-Al ratio. The solid fraction of the products in relation only to the mass of polypropylene was around 10 wt.% with the changing Ni-Al ratios. The solid fraction presented in this paper included the residue, char and coke after the pyrolysis–gasification of polypropylene. It should be noted that the investigation of different catalysts in relation to hydrogen production from the pyrolysis–gasification of polypropylene had no influence on the pyrolysis of polypropylene, since pyrolysis conditions were maintained for each experiment. The comparison of hydrogen production from pyrolysis–gasification of polypropylene with or without catalyst was investigated in our previous work [4], where hydrogen production was significantly improved in the presence of catalyst.

The non-condensed gases obtained from the pyrolysis–gasification of polypropylene were analysed with packed column GC, and the compositions are shown in Table 3. The results indicate that the CO content decreased from 27.8 to 23.9 vol.%, the CO₂ content increased from 5.5 to 8.1 vol.%, H₂ concentration increased from 62.7 to 66.6 vol.%, when the molar ratio of Ni-Al was increased from 1:4 to 1:1.

The potential H₂ production in the presence of Ni-Al catalyst is presented in Fig. 3. The maximum theoretical amount of H₂ produced from polypropylene–steam gasification has been estimated to be 42.9 g/100 g of polypropylene [2]. In this paper, the theoretical potential H₂ production corresponded to the maximum hydrogen production for the 100% conversion of the hydrogen contained in the polypropylene polymer, i.e. 42.9 g/100 g polypropylene. It is shown from Fig. 3 that the potential H₂ production was increased from 48.8 to 57.7 wt.% when the Ni-Al molar ratio was increased from 1:4 to 1:1. The increasing H₂ and CO₂ concentration and the decreasing of CO concentration in the produced gas is most likely to be due to the promotion of the water gas shift (WGS) reaction (reaction (1)), in the presence of the more reducible NiO present in the Ni-Al (1:1) catalyst.

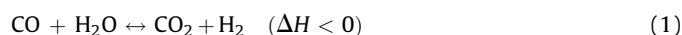


Table 2

Mass balances of the pyrolysis–gasification of polypropylene (PP) with different catalysts calcined at 750 °C.

	Catalyst							
	Ni-Al (1:4)	Ni-Al (1:2)	Ni-Al (1:1)	Ni-Mg-Al (1:1:4)	Ni-Mg-Al (1:1:2)	Ni-Mg-Al (1:1:1)	Ni-Cu-Al (1:1:1)	Ni-Cu-Mg-Al (1:1:1:3)
Mass balance in relation to PP + water								
Gas/(PP + water) (wt.%)	88.6	96.0	92.5	95.9	100.3	99.1	99.7	95.8
Solid/(PP + water) (wt.%)	5.3	2.8	5.6	3.1	0.6	0.5	0.1	0.1
Mass balance (wt.%)	93.9	98.7	98.1	99.0	100.8	99.6	99.8	95.9
Carbon balance (wt.%)	92.7	93.4	94.3	97.0	100.1	99.5	88.1	92.0
Mass balance in relation to PP only								
Gas/PP (wt.%)	194.7	212.2	219.2	216.8	229.5	245.1	199.6	197.9
Solid/PP (wt.%)	11.6	6.1	13.3	6.9	1.3	1.3	0.2	0.2
Mass balance (wt.%)	206.3	218.3	232.4	223.7	230.8	246.3	199.8	198.1
Reacted water (g)	1.20	1.21	1.30	1.26	1.29	1.40	1.00	1.07

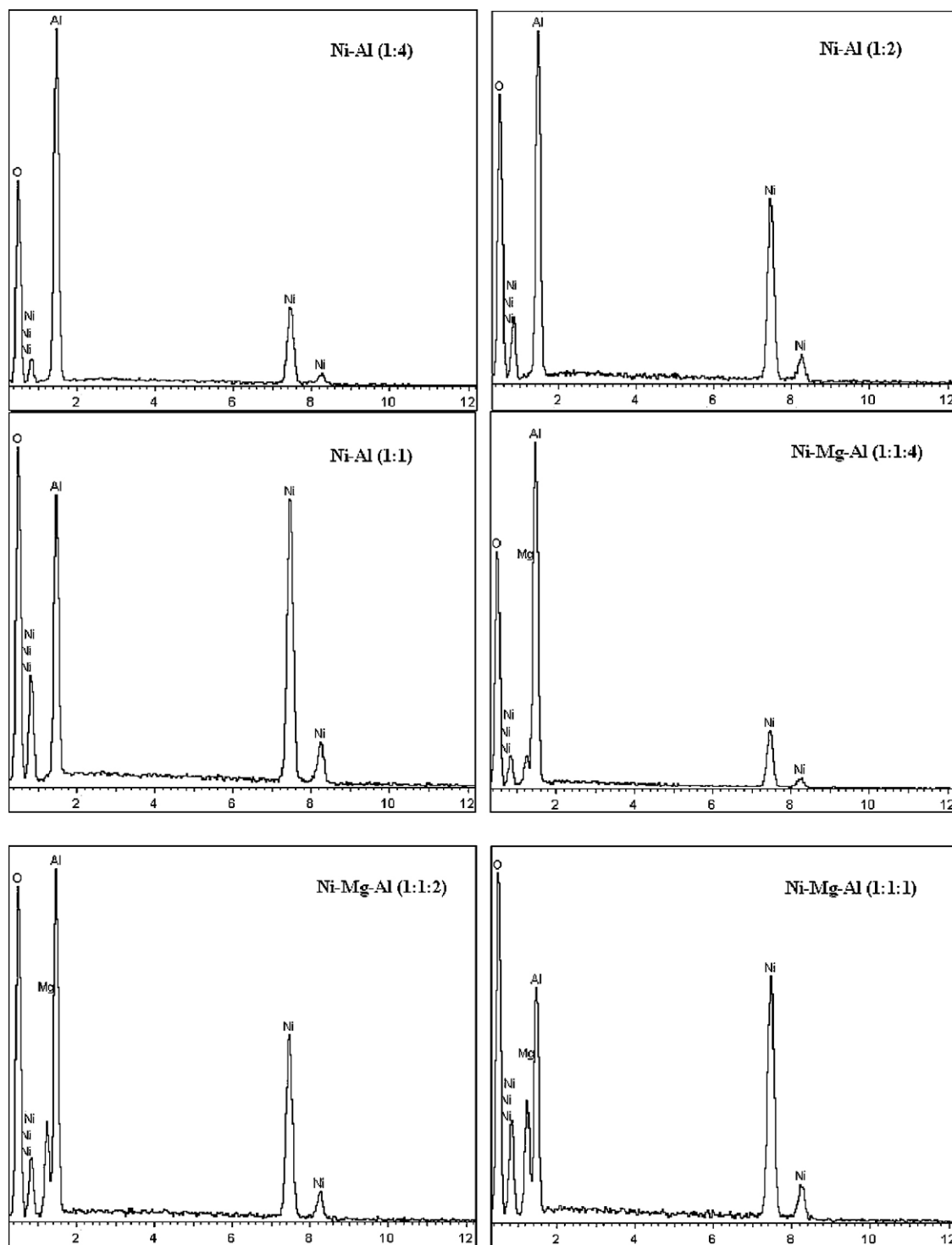


Fig. 2. EDXS results of fresh Ni-Al (1:1), Ni-Al (1:2), Ni-Al (1:4), Ni-Mg-Al (1:1:1), Ni-Mg-Al (1:1:2), Ni-Mg-Al (1:1:4) catalyst.

Table 3

Gas composition in the produced gases from different catalyst calcined at 750 °C.

Gas	Catalyst							
	Ni-Al (1:4)	Ni-Al (1:2)	Ni-Al (1:1)	Ni-Mg-Al (1:1:4)	Ni-Mg-Al (1:1:2)	Ni-Mg-Al (1:1:1)	Ni-Cu-Al (1:1:2)	Ni-Cu-Mg-Al (1:1:1:3)
CO	27.8	25.7	23.9	29.0	28.4	27.7	26.2	27.4
H ₂	62.7	64.0	66.6	60.8	61.2	62.2	61.1	62.2
CO ₂	5.5	6.4	8.1	6.2	6.4	7.0	8.9	5.8
CH ₄	3.2	3.3	1.5	3.2	3.1	2.9	3.2	3.8
C ₂ –C ₄	0.8	0.6	0.0	0.8	0.9	0.1	0.5	0.9

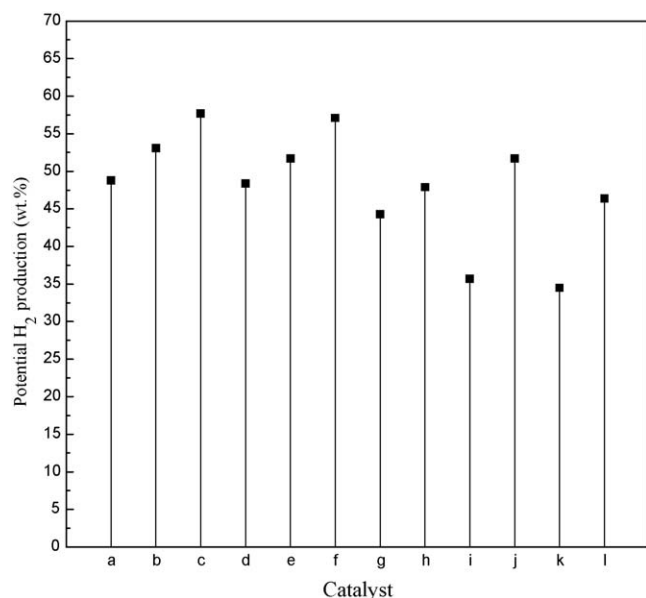


Fig. 3. Potential H₂ production from pyrolysis-gasification of polypropylene with different catalyst (a) Ni-Al (1:4); (b) Ni-Al (1:2); (c) Ni-Al (1:1); (d) Ni-Al-Mg (1:1:4); (e) Ni-Mg-Al (1:1:2); (f) Ni-Mg-Al (1:1:1); (g) Ni-Cu-Al (1:1:2); (h) Ni-Cu-Mg-Al (1:1:1:3); ((a)–(h) are calcined at 750 °C); (i) Ni-Al (1:4); (j) Ni-Al (1:1); k: Ni-Al-Mg (1:1:4); l: Ni-Mg-Al (1:1:1) ((i)–(l) are calcined at 850 °C).

The higher proportion of the NiO phase for the Ni-Al (1:1) catalyst was shown in Fig. 1. It is suggested that during the gasification process, the reducible environment (H₂ and CO) will reduce the non-reduced catalyst, and the Ni phase is the catalytic site for the gasification process [13]. Therefore, it seems that the catalytic activity of the Ni-Al catalyst has been improved with a higher Ni content. The increasing catalytic ability of the Ni-Al

catalyst with increasing Ni content was also reported by Al-Ubaid and Wolf [15], while they were using Ni-Al catalyst for the steam reforming of methane.

From Table 3, it should be pointed out that any C₂–C₄ hydrocarbon gases obtained with the Ni-Al (1:1) catalyst could not be detected by the GC. It is suggested that nearly all the large molecular compounds were cracked into H₂, CO, CO₂ and CH₄ gases in the presence of the highly catalytically active Ni-Al (1:1) catalyst.

3.1.3. Investigation of reacted Ni-Al catalyst

The reacted Ni-Al catalysts were analysed by TPO experiments. The TGA–TPO and DTG–TPO results are shown in Figs. 4 and 5, respectively.

Fig. 4 shows that the mass of reacted catalyst reduced first, then increased (especially Ni-Al (1:1)), and finally decreased to a stable content. It is suggested that the mass decreasing during the temperature range 0–100 °C was due to water vaporization. The final decrease of the mass should be due to the combustion of deposited coke on the catalyst. The phenomenon of mass increasing in the TGA–TPO result might be due to the oxidation of metallic Ni, since the Ni phase was observed from the XRD analysis (Fig. 1). And compared to other Ni-Al catalysts, Ni-Al (1:1) catalyst shows higher mass increasing peak (Fig. 4), also proved by XRD analysis.

From the DTG–TPO results (Fig. 5), it is indicated that two oxidation peaks of coke were observed at the temperature about 500 and 610 °C for the Ni-Al (1:4) and Ni-Al (1:2) catalyst. It is suggested that two types of carbons were formed on the surfaces of the reacted catalysts. The lower oxidation peak might be assigned to monoatomic carbon [16]. The higher oxidation peak could be assigned to filamentous carbon [17]. The filamentous carbons formed on the catalyst surface were observed by the SEM analysis (Fig. 6). However, the first oxidation peak (around 500 °C) disappeared for the Ni-Al catalyst with a molar ratio of 1:1. It is

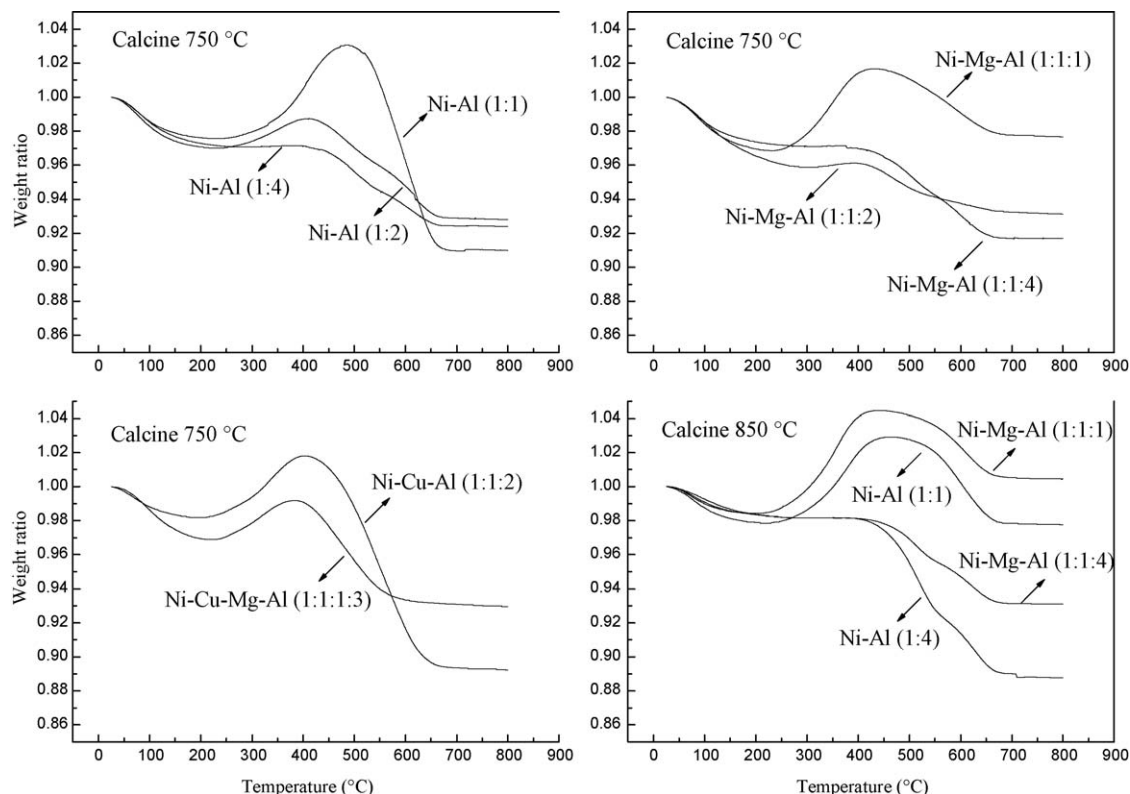


Fig. 4. TGA–TPO results of pyrolysis-gasification of polypropylene with various catalysts.

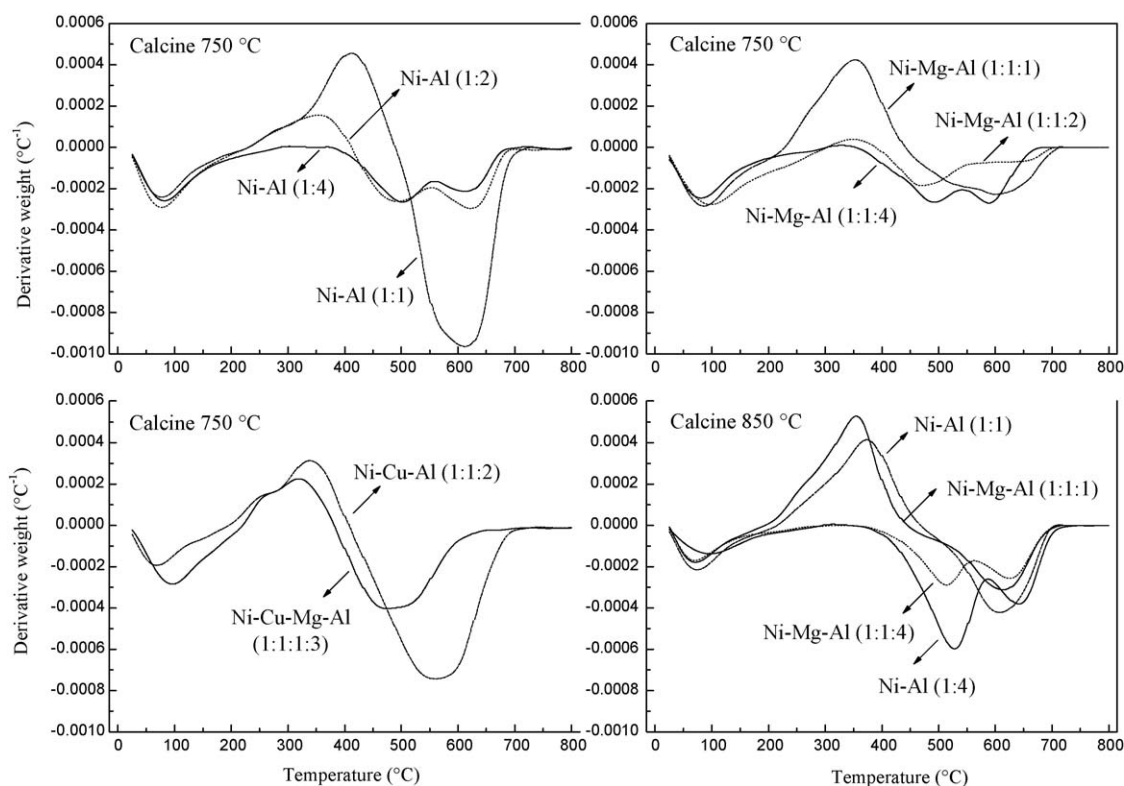
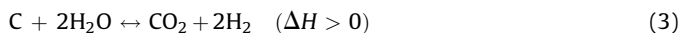
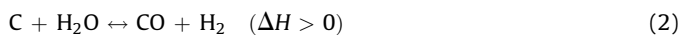


Fig. 5. DTG-TPO results of pyrolysis-gasification of polypropylene with various catalysts.

suggested that the monoatomic carbon might be gasified with the higher catalytic activity of Ni-Al (1:1) catalyst through the reactions (2) and (3).



However, large amounts of carbon were deposited on the Ni-Al (1:1) catalyst shown by the high intensity of the second oxidation peak in DTG-TPO results (Fig. 5), while the coke amount deposited on the Ni-Al (1:4) and Ni-Al (1:2) catalysts were shown to be comparatively lower. It is also relevant that metallic Ni with a diameter around 20–100 nm might be observed from the SEM analysis (Fig. 6). Metallic Ni was also shown to be present by the TEM-EDXS analysis of the reacted Ni-Al (1:1) catalyst (Fig. 7). From Fig. 7, filamentous carbons and metallic Ni in the Ni-Al (1:1) catalyst were observed from the TEM-EDXS analysis. The diameter of the filamentous carbons was around 20 nm.

3.2. The influence of Mg or Cu addition to the Ni-Al catalyst

From the above discussion, it is suggested that the Ni-Al (1:1) catalyst has a high catalytic activity in relation to hydrogen production from the pyrolysis-gasification of polypropylene. However, the high amount of coke deposited on the catalyst indicates that modification of the Ni-Al catalyst via metal addition to the catalyst may improve catalytic activity. It has been reported that magnesium has an ability to enhance steam gasification of carbon or carbon precursors formed on the catalyst during the reforming of hydrocarbons [18]. The addition of Mg into the Ni-Al catalyst by co-precipitation has been studied by Garcia et al. [13], for the steam gasification of biomass at 700 °C. They concluded that a NiMgAl₂O₅ catalyst showed the best performance corresponding to the highest catalytic activity and stability. Some

studies have shown that the addition of Cu to the Ni-Al catalyst may improve the catalyst performance for methane decomposition [19–21]. In this paper, the addition of Mg or Cu to the Ni-Al catalyst was also examined for the production of hydrogen from pyrolysis-gasification of polypropylene.

It seems that the BET surface area of the Ni-Al catalyst was reduced by the addition of Mg. For example, with the Ni content in the catalyst constant, the addition of Mg into the catalyst reduced the BET surface area of the catalyst from 155 m² g⁻¹ (Ni-Al (1:2)) to 99 m² g⁻¹ (Ni-Mg-Al (1:1:1)).

The mass balances for the pyrolysis-gasification of polypropylene in the presence of the Ni-Mg-Al catalysts are shown in Table 2. It is indicated that the amount of reacted water and the gas yield increased with the addition of Mg into Ni-Al catalyst. From Table 2, the amount of reacted water increased from 1.21 to 1.4 (g water/g polypropylene), and the gas yield responding only to the mass of polypropylene increased from 212.2 to 245.1 wt.%, when the catalyst was changed from Ni-Al (1:2) to Ni-Mg-Al (1:1:1).

The concentrations of gases produced from the pyrolysis-gasification of polypropylene in the presence of Ni-Mg-Al catalyst are also shown in Table 3. It is shown that the H₂ concentration decreased with the introduction of Mg into the Ni-Al catalyst. Since the concentration of H₂ gas was higher than 62.7 vol.% for the Ni-Al catalyst, when the H₂ concentration with various Ni-Mg-Al catalyst was less than 62.2 vol.%. The CO concentration increased, and the concentrations of CO₂ and hydrocarbon gases showed slight changes, when Mg was added to the Ni-Al catalyst. From Fig. 3, the potential H₂ production increased slightly, when the Ni-Al (1:2) was changed to Ni-Mg-Al (1:1:1) catalyst.

It seems that with the introduction of Mg into the Ni-Al catalyst, the catalytic activity of the catalyst in relation to H₂ production was not significantly improved, however, the steam gasification (reaction (2) and (3)) might be improved to generate higher gas yield. The TGA-TPO and DTG-TPO results showed that the deposited carbon on the surface of the catalyst was reduced by

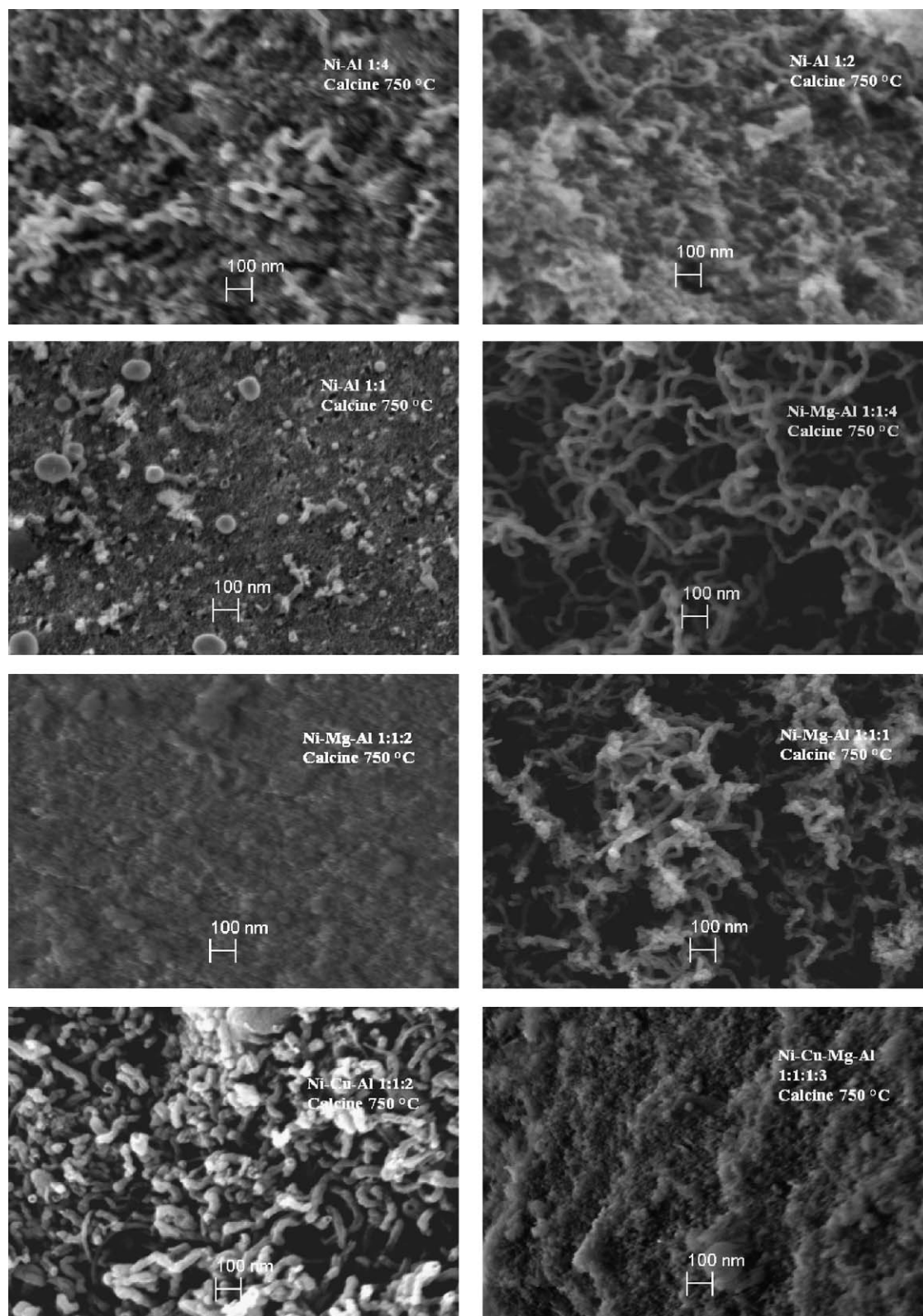


Fig. 6. SEM results of the reacted catalysts calcined at 750 °C.

the introduction of Mg into Ni-Al catalyst (Figs. 4 and 5). For example, with the addition of Mg into the Ni-Al (1:1) catalyst structure (while maintaining the Ni content), the carbon oxidation peak (around 610 °C) from DTG-TPO experiment for Ni-Mg-Al (1:1:1) was reduced compared to the Ni-Al (1:2) catalyst (Fig. 5). It

is pointed out that the two oxidation peaks were also observed for the Ni-Mg-Al (1:1:4) and Ni-Mg-Al (1:1:2) catalysts.

Different Ni contents in the Ni-Mg-Al catalyst were also studied in this paper. It appeared that the influence of the Ni content in the Ni-Mg-Al catalyst was similar to the Ni-Al catalyst discussed

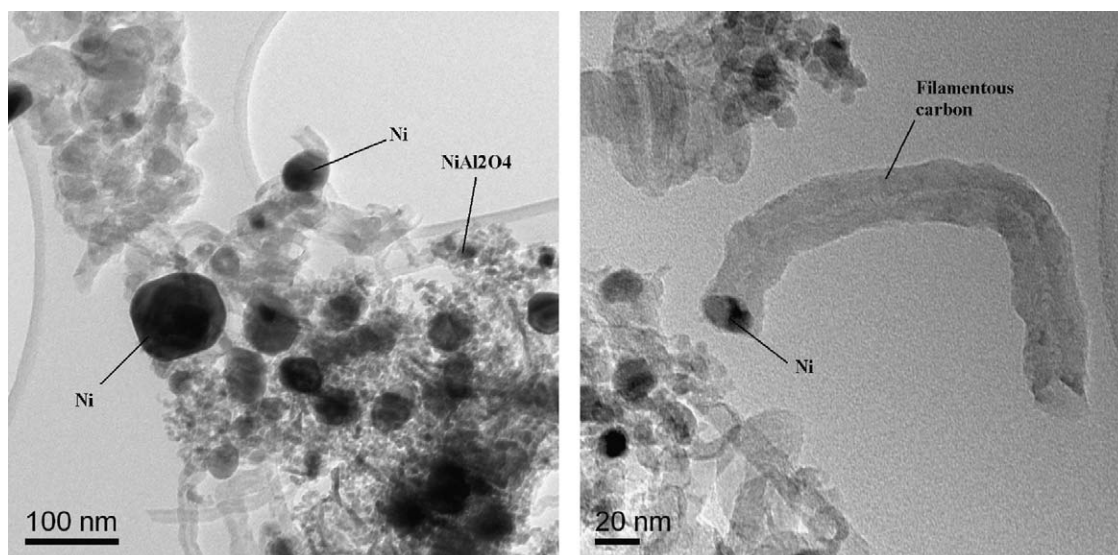


Fig. 7. TEM results of the reacted Ni-Al (1:1) catalyst calcined at 750 °C.

before. Increasing the Ni content resulted in a higher catalytic ability of the Ni-Mg-Al catalyst, such as higher gas yield, more consumed water, and the higher H_2 concentration. For the coked Ni-Mg-Al (1:1:1) catalyst with high Ni content, the DTG–TPO experiment showed that a mass increasing peak occurred in the DTG curve around 350 °C, which might be due to the oxidation of the metallic Ni (Fig. 5).

The results of the pyrolysis–gasification of polypropylene with Ni-Cu-Al (1:1:2) and Ni-Cu-Mg-Al (1:1:1:3) were also investigated in this paper. It is shown in Table 2 that the lower gas yields and consumed water amount were observed compared with the Ni-Al or Ni-Mg-Al catalyst. In addition, the potential H_2 production for the Ni-Cu-Al (1:1:2) was also lower than the Ni-Al (1:4) catalyst (Fig. 3). From Fig. 3, it is also suggested that the catalytic activity of Ni-Cu-Mg-Al (1:1:1:3) was reduced with lower potential H_2 production, compared to the Ni-Mg-Al (1:1:4) catalyst. This might be due to the addition of Cu, since Cu was suggested to be not an active site during the gasification process [22]. Furthermore, the comparatively lower catalytic activity of the Ni-Cu-Al or Ni-Cu-Mg-Al catalyst might be due to its lower BET surface area, which was around $70 \text{ m}^2 \text{ g}^{-1}$ (Table 1). It is suggested that with the addition of Mg into the Ni-Cu-Al catalyst; the catalytic performance was improved in relation to the production of hydrogen and prohibition of coke formation (Figs. 3 and 5). The filamentous carbons formed on the Ni-Al catalyst with the addition of Mg or Cu were also observed from SEM analysis (Fig. 6).

3.3. The influence of calcination temperature

Calcination temperature of the catalyst during the preparation process plays an important role in the catalytic activity of the derived catalyst [23,24]. In this paper, the investigation of calcination temperature at 750 and 850 °C was carried out in relation to the production of hydrogen from the pyrolysis–gasification of polypropylene. Four catalysts, Ni-Al (1:4), Ni-Al (1:1), Ni-Mg-Al (1:1:4) and Ni-Mg-Al (1:1:1) were studied. Compared to the catalysts calcined at 750 °C, the catalysts prepared at the higher calcination temperature of 850 °C, showed lower BET surface areas (Table 1). From Table 1, it can be observed that the BET surface area of Ni-Al (1:4) catalyst was reduced from 143 to $88 \text{ m}^2 \text{ g}^{-1}$, when the calcination temperature was increased from 750 to 850 °C.

The mass balances of the experiments with the catalysts calcined at 850 °C are shown in Table 4. The data showed that only 0.9 (g water/g polypropylene) water was consumed by using Ni-Al (1:4) catalyst calcined at 850 °C, while 1.2 (g water/g polypropylene) water was reacted using Ni-Al (1:4) catalyst calcined at 750 °C. The reacted water amount for the other studied catalysts calcined at 850 °C was also reduced significantly compared to those calcined at 750 °C (Table 4). It is suggested that the catalytic ability was reduced when the calcined temperature was increased from 750 to 850 °C. The hydrogen concentration and the potential hydrogen production

Table 4

Mass balances of the results with different catalysts calcined at 850 °C.

	Catalyst			
	Ni-Al (1:4)	Ni-Al (1:1)	Ni-Mg-Al (1:1:4)	Ni-Mg-Al (1:1:1)
Mass balance in relation to PP + water				
Gas/(PP + water) (wt.%)	97.3	93.0	88.1	91.9
Solid/(PP + water) (wt.%)	1.7	4.0	3.6	2.8
Mass balance (wt.%)	98.9	97.0	91.7	94.7
Carbon balance (wt.%)	105.4	94.5	98.9	90.9
Mass balance in relation to PP only				
Gas/PP (wt.%)	185.8	209.5	173.4	195.8
Solid/PP (wt.%)	3.2	9.0	7.1	6.0
Mass balance (wt.%)	189.0	218.5	180.4	201.8
Reacted water (g)	0.9	1.3	1.0	1.1

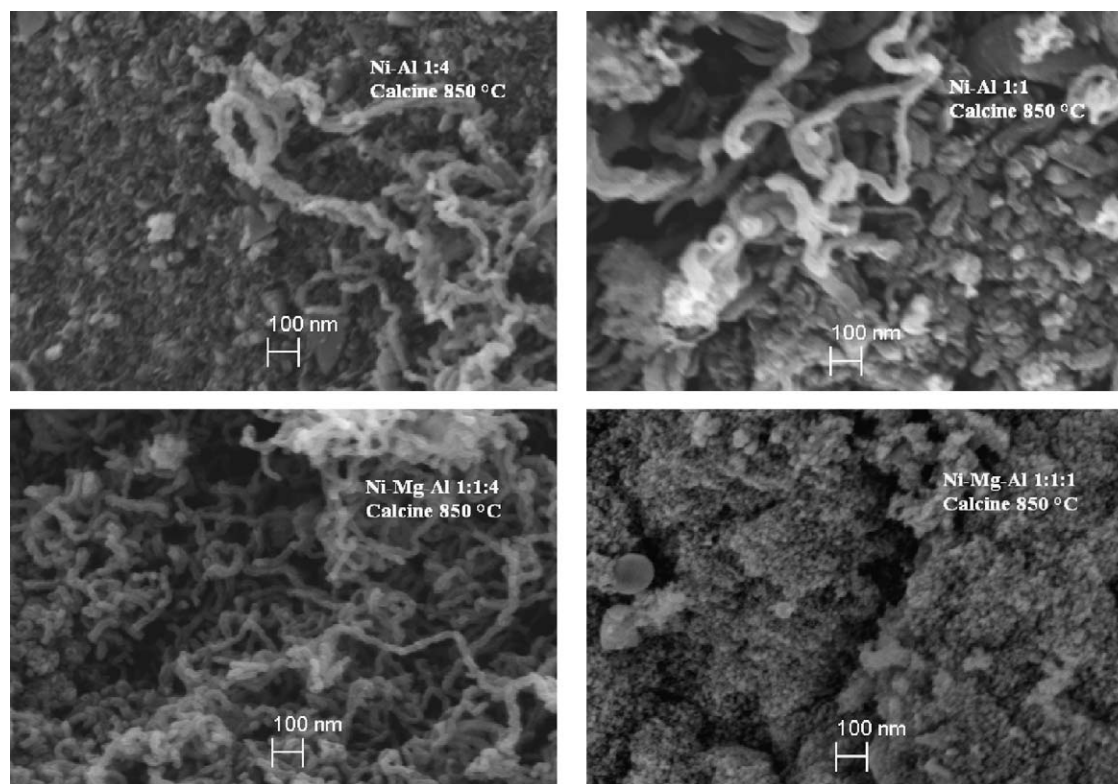


Fig. 8. SEM results of the reacted catalysts calcined at 850 °C.

were also shown to be reduced by the increasing calcination temperature (Table 5 and Fig. 3). For example, the potential hydrogen production reduced from 48.8 to 35.7 wt.% for Ni-Al (1:4), from 57.7 to 51.7 wt.% for Ni-Al (1:1), from 48.4 to 34.5 wt.% for Ni-Mg-Al (1:1:4), and from 57.1 to 46.4 wt.% for Ni-Mg-Al (1:1:1) catalyst, when the calcination temperature was increased from 750 to 850 °C.

The TPO experiment of the coked catalyst calcined at 850 °C was also determined. The TGA–TPO and DTG–TPO results are shown in Figs. 4 and 5, respectively. Fig. 5 shows that two peaks of carbon combustion were also found from the DTG–TPO results for the Ni-Al (1:4) and Ni-Mg-Al (1:1:4) catalyst calcined at 850 °C. It is suggested that the types of carbons deposited on the catalyst surface after the pyrolysis–gasification of polypropylene was slightly influenced by the calcination temperature. Furthermore, a mass-increase peak from the DTG–TPO result was also observed for the Ni-Al (1:1) and Ni-Mg-Al (1:1:1) catalyst. It is suggested that metallic Ni was also formed for the catalysts calcined at 850 °C. From the SEM analysis of the reacted catalysts prepared at the calcination temperature of 850 °C (Fig. 8), filamentous carbons were observed. These filamentous carbons would be related to the high oxidation peak (around 610 °C) observed in the DTG–TPO results (Fig. 5).

Table 5

Gas composition in the produced gases from different catalyst calcined at 850 °C.

Gas	Catalyst			
	Ni-Al (1:4)	Ni-Al (1:1)	Ni-Mg-Al (1:1:4)	Ni-Mg-Al (1:1:1)
CO	25.0	24.9	26.3	28.2
H ₂	55.3	63.7	56.0	61.8
CO ₂	6.8	8.8	6.6	7.0
CH ₄	6.3	2.4	5.3	3.0
C ₂ –C ₄	6.7	0.1	5.9	0.02

4. Conclusions

In this paper, the molar ratio of Ni-Al, the addition of Mg or Cu into the Ni-Al catalyst structure and the calcination temperature of the catalyst were investigated in relation to the production of hydrogen from the pyrolysis–gasification of polypropylene.

The non-reduced catalyst appeared to be reduced during the experiment, especially the catalyst with high Ni content. It is suggested that the non-reduced catalyst could be used in the gasification process for hydrogen production, in order to reduce the cost of pre-reduction of catalyst.

The increasing Ni content in the Ni-Al and Ni-Mg-Al catalyst structure results in a higher catalytic activity during the pyrolysis–gasification of polypropylene. Increasing the molar ratio of the Ni-Al catalyst from 1:4 to 1:1 resulted in an increase in gas yield related to the mass of polypropylene, from 194.7 to 219.2 wt.%, and the hydrogen concentration in the produced gases increased from 62.7 to 66.6 vol.%.

It is suggested that with the introduction of Mg into the Ni-Al catalyst structure, the cracking ability of the catalyst to generate hydrogen was not improved. However, the steam gasification of the polypropylene might be significantly improved with the introduction of Mg into Ni-Al catalyst. Since, the amount of water reacted during the gasification process was increased, when the catalyst was changed from Ni-Al (1:1) to Ni-Mg-Al (1:1:1). In addition, a lower amount of coke was deposited on the catalyst with Mg present in the catalyst structure, observed from the TPO analysis. In addition, it was suggested that the addition of Cu into the Ni-Al catalyst structure might not be suitable for hydrogen production from the pyrolysis–gasification of polypropylene.

The investigation of calcination temperature showed that higher calcination temperatures (850 °C) reduced the catalytic ability of the Ni-Al or Ni-Mg-Al catalyst resulting in a lower amount of consumed water and a lower hydrogen production, when compared with the lower (750 °C) calcination temperature.

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